(19) World Intellectual Property Organization International Bureau



. | 1884 | 1885 | 1884 | 1884 | 1884 | 1885 | 1885 | 1885 | 1885 | 1885 | 1885 | 1885 | 1885 | 1885 | 1885 | 1

(43) International Publication Date 2 August 2001 (02.08.2001)

PCT

(10) International Publication Number WO 01/54878 A1

- (51) International Patent Classification⁷: B29C 33/38, 45/27, B22F 5/00 // B29C 33/02, 45/26, 45/73, B22F 3/26
- (21) International Application Number: PCT/CA01/00092
- (22) International Filing Date: 29 January 2001 (29.01.2001)
- (25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

09/493,149

28 January 2000 (28.01.2000) US

- (71) Applicant (for all designated States except US): MOLD-MASTERS LIMITED [CA/CA]; 233 Armstrong Avenue, Georgetown, Ontario L7G 4X5 (CA).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): GELLERT, Jobst, U. [CA/CA]; 7A Prince Street, Glen Williams, Ontario L7G 2X1 (CA). BELHADJHAMIDA, Hakim [CA/CA]; 506 Donalds Avenue, Toronto, Ontario M4J 3S4 (CA).
- (74) Agent: BERESKIN & PARR; 40 King Street West, Box 401, 40th Floor, Toronto, Ontario M5H 3Y2 (CA).

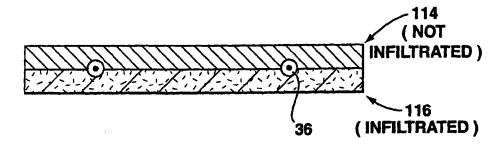
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: MOULD HAVING EMBEDDED HEATING ELEMENT AND IMPROVED THERMAL CONDUCTIVITY



(57) Abstract: The present invention provides improved heated manifolds, heaters and nozzles for injection molding, having a high strength metal skeleton infiltrated with a second phase metal having higher thermal conductivity. Also disclosed is method of forming a manifold, heater or nozzle preform and infiltrating the preform with a highly thermally conductive material. The invention also provides a method of simultaneously infiltrating and brazing injection molding components of similar or dissimilar materials together.

01/54878 A1

10

15

20

30

MOULD HAVING EMBEDDED HEATING ELEMENT AND IMPROVED THERMAL CONDUCTIVITY

FIELD OF THE INVENTION

The invention relates to injection molding and more particularly to an improved heating element, having high strength and high thermal conductivity, for use in an injection molding apparatus.

BACKGROUND OF THE INVENTION

As is well known in the art, hot runner injection molding systems have a manifold to convey the pressurized melt from the inlet at a molding machine to one or more outlets, each of which lead to a nozzle which, in turn, extends to a gate to an injection mold cavity. Manifolds and nozzles have various configurations, depending upon the number and arrangement of the cavities. It is known to be desirable to provide a means of heating the manifold and/or nozzles to maintain a desired temperature distribution across the manifold and/or nozzle. Various means of heating manifolds and nozzles are known. For instance, a manifold can have an electrical heating element integrally cast or brazed into the manifold, as described respectively in U.S. Patent Nos. 4,688,622 to Gellert and 4,648,546 to Gellert, a cartridge heater can be cast in the manifold, as disclosed in U.S. Patent No. 4,439,915 to Gellert, or a plate heater can be positioned adjacent the manifold to provide heat thereto, as disclosed in pending U.S. application serial no. 09/327,490, filed June 8, 1999 and concurrently owned herewith. Similarly, a nozzle may have an integral heater element brazed therein, as shown in U.S. Patent No. 4,557,685 to Gellert, may have a heated sleeve disposed around the nozzle, as shown in U.S. Patent Nos. 5,411,392 and 5,360,333 to Von Buren and Schmidt, respectively, or may employ a film heater as shown in U.S. Patent No. 5,973,296.

The high pressures and temperatures and numerous cycles experienced in injection molding systems requires manifold, nozzle and heater components to be fabricated of high strength materials, typically high

10

15

20

25

30

strength tools steels, such as H13. Such materials also typically have good corrosion resistance properties, which is beneficial as is well known in the art. Tools steels, however, have poor thermal conductivity, making exacting control over runner and gate temperatures difficult. Materials such as copper, however, though highly thermally conductive, typically have low strength and hardness in comparison to tool steels. Further, copper and its alloys also have a very poor corrosion resistance. Though, other thermally conductive materials are known, such as refractory alloys like molybdenum and tungsten, these materials can be prohibitively expensive, not to mention difficult to machine.

For some applications, it is known that high strength and high thermal conductivity can be achieved through the use of so-called 'metal infiltration' techniques, wherein a porous skeleton composed of a high strength metal is infiltrated by a thermally conductive metal to yield a two-phase composite part having improved characteristics over both component metals. United States Patent No. 4,710,223 to Matejcezyk discloses an infiltration method for achieving super erosion and high-temperature resistance in rocket nozzles and reaction engines by infiltrating a refractory metal, such as molybdenum or tungsten, with copper or an alloy of copper.

United States Patent No. 5,775,402 to Sachs discloses a process of so-called 'three dimensional printing' whereby a metal powder/binder mixture is deposited in layers by computer-controlled machinery to fabricate the complexly-shaped preform layer-by-layer. The preform is then sintered and infiltrated according to known techniques to achieve a two-phase material having good strength and temperature conductivity. Sachs however, requires complex programming and machinery to achieve the preform.

There is a need for achieving injection molding manifold, nozzle and heater components with increased thermal conductivity without sacrificing strength and, further, there is a need for achieving such parts through simpler fabrication techniques.

As noted above, injection molding components can be heated

10

15

20

25

30

by an integral heater, such as disclosed in U.S. Patent No. 4,648,546 to Gellert. Typically, a brazing or bonding step is required to join the heater element to the component, to obtain good heat transfer characteristics between the element and the manifold, nozzle and/or heater. This brazing step, however, requires additional effort and time in the tooling process.

Accordingly, there is also a need for a reduction in the number of manufacturing and tooling operations required in making high strength and highly thermally conductive manifolds, nozzles and heaters.

SUMMARY OF THE INVENTION

In a first embodiment, the present invention provides an assembly for heating an injection molding component, the assembly comprising a body and a heating element for controllably heating the body, the heating element attached to the body, wherein the body is made of a parent metal, the parent metal being at least partially infiltrated with a second metal, the second metal having a higher thermal conductivity than the parent metal.

In a second embodiment, the present invention provides a hot runner injection molding apparatus comprising a melt conveying system, the system having a melt distribution manifold having at least one melt passage for transferring melt from a source of pressurized melt, and at least one injection nozzle having a melt bore therethrough, the melt bore in fluid communication with the at least one manifold melt passage, at least one mold cavity adjacent the at least one nozzle, the mold cavity in fluid communication with the melt bore of the at least one nozzle, a body for heating at least a portion of the melt conveying system, the body having a heating element attached thereto, the heating element capable of heating at least a portion of the body, wherein at least a portion of the body is made of a parent metal, the parent metal being at least partially infiltrated with a second metal having a higher thermal conductivity than the parent metal.

In a third embodiment, the present invention provides a process for fabricating an injection molding component having an electrical heating

15

20

25

30

element attached thereto, the process comprising the steps of: contacting the electrical heating element with a powdered metal preform having at least partial open porosity, the powdered metal preform being composed of a first metal; contacting the preform adjacent a region of the open porosity with a mass of a second metal, the second metal having higher thermal conductivity than the first metal; heating the preform, the heating element and the mass so as to cause the second metal to at least partially infiltrate the open porosity of the preform and at least partially join the heating element to the preform when cooled.

In a fourth embodiment, the present invention provides a process for fabricating a metal part having at least two components, the process comprising the steps of: making a powdered preform of a first component, the preform having at least partial open porosity; contacting a second component with the preform of the first component; and infiltrating the open porosity of preform with a second metal wherein the second component is brazed to the first component by the second metal substantially contemporaneously with the infiltration step.

In a fifth embodiment, the present invention provides a process for fabricating a metal part having at least two components, the process comprising the steps of: making a powdered preform of a first component, the preform having at least partial open porosity; contacting a second component with the preform of the first component to form an assembly thereof; contacting the preform first component with a mass of a metal infiltrant; controllably heating the assembly and the metal infiltrant to melt the metal infiltrant; holding the assembly and the metal infiltrant at temperature until the open porosity of the preform of the first component is at least partially infiltrated by the metal infiltrant and the second component is at least partially brazed to the first component by the metal infiltrant; and controllably cooling the assembly to solidify the metal infiltrant.

In a sixth embodiment, the present invention provides a process for fabricating an injection molding component, the process comprising the steps of: mixing a powdered tool steel with a binder to form an admixture;

20

25

injecting the admixture into a preform; debinderizing the preform; partially sintering the preform to achieve 40% to 10% volume open porosity therein; contacting the preform with a metal infiltrant, the metal infiltrant having high thermal conductivity; controllably heating the preform and the metal infiltrant to at least the melting temperature of the metal infiltrant; holding the preform and the metal infiltrant at temperature until the porosity of the first component is at least partially infiltrated by the metal infiltrant; and cooling the preform to solidify the metal infiltrant and yield the injection molding component.

10 BRIEF DESCRIPTION OF THE DRAWINGS

For a better understanding of the present invention, and to show more clearly how it may be carried into effect, reference will now be made by way of example to the accompanying drawings. The drawings show articles made according to preferred embodiments of the present invention, in which:

Figure 1 is a sectional side view of a portion of a typical injection molding system incorporating an infiltrated heated manifold in accordance with the present invention;

Figure 2 is an exploded isometric view, from the underside, of the heated manifold assembly of Figure 1;

Figure 3 is a sectional view along the line 3-3 in Figure 2;

Figure 4 is a sectional side view of the heated nozzle of Figure 1;

Figure 5 is a sectional side view of the nozzle of Figure 4, shown prior to installation of the nozzle heating element;

Figure 6 is a representation of a photomicrograph of the infiltrated heated manifold of the device of Figure 1;

Figure 7 is a sectional side view of a portion of a typical injection molding system incorporating an infiltrated manifold heater plate assembly in accordance with an alternate embodiment of the present invention;

Figure 8 is an exploded isometric view of the heater plate assembly of Figure 7;

10

15

20

Figure 9 is an isometric view of the assembled heater plate assembly of Figure 7;

Figure 10 is an isometric view of an alternate embodiment of the heater plate assembly of Figure 7;

Figure 11 is a sectional view along the line 11-11 in Figure 10;

Figure 12 is a sectional side view of a typical injection molding system incorporating an infiltrated nozzle band heater assembly in accordance with an alternate embodiment of the present invention;

Figure 13 is an exploded view of a band heater and spring clamp according to one aspect of the embodiment of Figure 12;

Figure 14 is a sectional side view of a bimetallic band heater according to a second aspect of the embodiment of Figure 12;

Figure 15 is an isometric view of the green preform assembly of the heater plate of Figure 7;

Figure 16 is a sectional side view of a manifold heater wherein one plate is infiltrated and one plate is uninfiltrated;

Figure 17 is a sectional side view of a portion of a typical injection molding system incorporating a film heater element and infiltrated components in accordance with the present invention;

Figure 18 is an enlarged partial view of the film heater plate of the embodiment of Figure 17;

Figure 19 is a plan view of the film heater of Figure 17; and

Figure 20 is an enlarged sectional view of the band heater of Figure 12 employing a film heater element.

15

20

25

30

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

An injection molding system according to the present invention is shown in the Figures generally at M. Reference is first made to Figure 1, which shows a portion of molding system M having one or more steel nozzles 10 (only one is shown in Figure 1) to convey pressurized plastic melt through a melt passage 12 to a gate 14 leading to a cavity 16 in a mold 18. In this particular configuration, mold 18 includes a cavity plate 20 and a back plate 22 which are removably secured together by bolts 24. It will be understood that mold 18 may have a greater number of plates depending on the application, only plates 20, 22 are shown and described here, for ease of illustration.

Mold 18 is cooled by pumping cooling water through cooling conduits 26 extending in cavity plate 20 and back plate 22. An electrically heated, infiltrated melt distribution manifold 28 (preferably copper-infiltrated steel) is mounted between cavity plate 20 and back plate 22 by a central locating ring 30, positioned in a mating hole 30a in manifold 28, and insulative and resilient spacer members 32. Melt distribution manifold 28 has a cylindrical inlet portion 34 and is heated by an integral electrical heating element 36. An insulative air space 38 is provided between heated manifold 28 and the surrounding cooled cavity plate 20 and back plate 22. Melt passage 12 extends from a common inlet 40 in inlet portion 34 of manifold 28 and branches outward in manifold 28 to each nozzle 10 where it extends through a central melt bore 42 and then through an aligned central opening 44 in a torpedo 46 to one of gates 14.

Each nozzle 10 has an outer surface 48, a rear end 50, and a forward end 52. Nozzle 10 of this particular configuration is also heated by an integral electrical heating element 54 which has a spiral portion 56 extending around melt bore 42 and an external terminal 58 to which electrical leads 60 from a power source are connected. In other applications, heating element 36 and the melt itself may supply sufficient heat that a heating element is not required in nozzle 10. Nozzle 10 is seated in a well 62 in cavity plate 20 with a cylindrical locating flange 64 extending forwardly to a circular

20

25

30

locating shoulder 66 in well 62. Thus, an insulative air space 68 is provided between inner surface 70 of well 62 and outer surface 48 of nozzle 10 to provide thermal separation between heated nozzle 10 and the surrounding cooled mold cavity 16. In this embodiment, melt bore 42 has an enlarged portion with a threaded inner surface 72 to form a threaded seat 74 at its forward end 52. In this particular configuration, well 62 has a smaller central portion 76 which extends forwardly past air space 68 and tapers inwardly to gate 14. A small circular seat 78 extends in mold cavity 16 around a central portion 76 of well 62. It will be understood that nozzle 10 may have other configurations for different gating arrangements, depending on the gating desired for a particular application.

Referring to Figures 2 and 3, manifold 28 comprises a substantially planar body 80 having a groove 82 in a face 84 of body 80 for receiving electrical heater element 36. The configuration of groove 82 in face 84 is designed to provide manifold 28 with a desired temperature distribution depending on the application. Element 36 is brazed (indicated by reference numeral 86) into groove 82 in face 84. Such brazing may be performed according to U.S. Patent No. 4,648,546 to Gellert, incorporated herein by reference, or by other known brazing techniques, i.e. as separate and distinct operations after the infiltration of manifold 28 has been completed, however, according to an aspect of the present invention such brazing is preferably achieved simultaneously with the infiltration of manifold 28, as will be described more fully below. Also, rather than brazing, element 36 may equally be joined to manifold 28 by other means, such as other mechanical attachment means, as are known in the art, such as by pressing element 36 into manifold 28 to create an interference, friction or deformation fit. Likewise, thermal spraying techniques may be employed to bond element 36 to manifold 28. The placement of heating element 36 can also be varied to locate it in an opposite face 88 of body 80, rather than face 84.

Referring to Figures 4 and 5, outer surface 48 of nozzle 10 has a generally spiralled channel 56 which extends around and along surface 48 of nozzle 10. A generally helical heating element 54 is received in the channel 56

15

20

25

30

and is embedded therein by brazing with a highly conductive material, such as nickel or copper, as is more fully described in United States Patent No. 4,557,685 to Gellert and incorporated herein by reference. As described in the '685 patent, and as may be seen in the Figures, the pitch of the spiralled channel 56 is not necessarily uniform, and is generally tighter in the vicinity of the areas where more heat is required.

Referring to Figure 6, manifold 28 comprises a metal skeleton 90 infiltrated by a second phase metal 92, the second phase metal 92 having a higher thermal conductivity than that of metal skeleton 90. Metal skeleton 90 is preferably a tool steel, and more preferably one of H13, M2 and D2, and most preferably H13. Second phase metal 92 is any highly thermally conductive metal and preferably copper, a copper alloy, silver or silver alloy, most preferably copper. In this application, including the claims appended hereto, it will be understood that the term "metal" is used to refer generally to both pure metals and alloys of metal(s). The process by which infiltration is achieved is described in more detail below.

In a second embodiment, nozzle(s) 10 in molding system M is also infiltrated by a second phase metal, in a manner as just described for manifold 28, and heater element 54 is also simultaneously brazed during infiltration into groove 56 by the second phase metal, as described below. In another aspect of this embodiment, nozzle 10 is infiltrated and manifold 28 is not.

In a third embodiment, the melt distribution manifold is heated externally, such as by a electrical heater plate adjacent the manifold, as described in U.S. pending application serial no. 09/327,490, filed June 8, 1999, which is concurrently owned herewith and the contents of which are incorporated by reference. Referring to Figure 7, in molding system M', a manifold 100 is mounted between cavity plate 20' and back plate 22' by a central locating ring 30', and a plurality of insulative spacers 32' are provided to facilitate maintenance of a temperature differential between melt distribution manifold 100 and mold 18'. An infiltrated heater plate 106 (preferably copper-infiltrated steel) according to the present invention is

WO 01/54878

10

15

20

25

30

removably mounted between nozzles 10' and melt distribution manifold 100 by screws 108 extending through heater plate 106, through holes 106a, and into manifold 100. A plurality of locating pins 110 extend from heater plate 106 into melt distribution manifold 100. Disposed within heater plate 106 is an electrical heating element 36'. Nozzle 10' is secured to heater plate 106 and melt distribution manifold 28' by bolts (not shown) extending through the melt distribution manifold 28' and heater plate 106.

- 10 -

PCT/CA01/00092

Referring to Figures 8 and 9, heater plate 106 comprises a planar body 112 having a front plate 114, having a groove 114a in an inner face 114b, and a rear plate 116, having a groove 116a in an inner face 116b. Heating element 36' is positioned intermediate plates 114 and 116, in a channel 118 formed by grooves 114a and 116a. A central bore 120 is provided in plates 114 and 116 to permit the passage of pressurized melt from manifold 100 to nozzle 10'. In other embodiments, the heater plate 106 can have a plurality of melt bores 120 extending therethrough to permit heater plate 106 to be mounted adjacent a plurality of nozzles 10'. Heating element 36' has terminal portions 36a extendably positioned from heater plate 106 for connection to the leads (not shown) of a controlled power supply (also not shown). The configuration of channel 118 in heater plate 106 is designed to provide and maintain the desired temperature distribution across heater plate 106, and therefore also manifold 100 by conduction from plate 106, for a given application. Although channel 118 is comprised of cooperating grooves 114a and 116a in plates 114 and 116, it will be understood by one skilled in the art that such cooperation is not essential and that the channel 118 can equally be provided entirely within plate 114 or 116, as desired.

Heating element 36' is preferably brazed into channel 118 and plates 114 and 116 are preferably brazed together at faces 114b to 116b. Such brazing may be performed according to the prior art, ie. as separate and distinct operations after the infiltration of plates 114 and 116 has been completed, however, according to an aspect of the present invention such brazing is preferably achieved simultaneously with the infiltration of plates 114 and 116, as will be described more fully below. Alternately to brazing,

plates 114 and 116 may be joined, and element 36' bonded therein and thereto, using any other mechanical or metallurgical means known in the art as suitable, such as friction fit or thermal spraying, etc.

It will be understood by one skilled in the art that the heater plate may be positioned elsewhere in relation to the manifold, such as the position shown in the Figure 17 embodiment described below.

5

10

15

20

25

30

Referring to Figures 10 and 11, it will be understood that other means of heating the manifold and heater plate are available. The heater elements 36 and 36' can be replaced by a heating passage 130 through which a heated fluid 132, such as oil, is circulated. In another embodiment (not shown), the heating element can be one or more conventional cartridge type resistance heaters or heat pipes extending into one or more bores in manifold 28 or heater plate 106, such as is described in U.S. Patent No. 4,500,279 to Devellian, incorporated herein by reference.

In a yet further embodiment, nozzle 10, rather than having integral heating element 54, has an external band heater, of the types disclosed in U.S Patent Nos. 5,411,392 to Von Buren and 5,360,333 to Schmidt, both of which are incorporated herein by reference. The construction of such band heaters will only briefly be described herein, though one skilled in the art will understand that the '392 and '333 patents fully describe the construction and operation of such heaters.

Referring to Figure 12, molding system M" is substantially identical to molding system M, except as will now be described. Nozzle 10" comprises a simple injection molding nozzle having a smooth outer surface 48". A band heater 200 is positioned snugly around nozzle 10". In operation, band heater 200 is connected to electrical leads 60" and provides heat by conduction to nozzle 10".

In one aspect of the embodiment of Figure 12, band heater 200 may comprise a heater of the type disclosed in U.S. Patent No. 5,411,392. Referring to Figure 13, in this aspect heater 200 comprises an annular heater 202 and an annular spring 204. Spring 204 is formed to be spring-like and to exert continuous pressure on heater 202 to urge heater 202 towards nozzle

20

25

30

10". Spring 204 is preferably formed into a diameter smaller than heater 202 so as to exert continuous tension therearound and to apply a preload to heater 202 for a secure assembly. Spring 204 preferably exerts continuous pressure and contact on heater 202 along the heaters entire length, however other configurations may be preferable for a given molding application. Ends 206 and 208 of spring 204 are spaced from each other to leave a gap 210 therebetween which permits leads 60" from heater 202 to exit, however, other configurations may be used, and spring 204 may completely surround heater 202 and overlap itself. Either or both of heater 202 and spring 204 can be comprised of a two-phase infiltrated metal, as shown in Figure 6 and described in further detail below, to enhance the strength and thermal conductivity of heater 200.

In a second aspect of this embodiment, band heater 200 may comprise a bi-metallic clamping system of the type described in U.S. Patent No. 5,360,333. Such a system provides a construction which holds heater 200 firmly on and around nozzle 10" without the need for additional clamping Referring to Figure 14, heater 200 is bi-metallic, formed by a means. cylindrical body or heater sheath 220 comprising a coaxial tube assembly with a cylindrical inner sleeve 222, a cylindrical outer sleeve 224 and a heater coil 226 positioned therebetween. Heater coil is electrically connected to leads 60" (not shown). As described in the '333 patent, inner sleeve 222 is formed from a material having a higher thermal expansion than outer sleeve 224. As will be understood by one skilled in the art, one or both of sleeves 222 and 224 can be fabricated of a two-phase infiltrated metal according to the present invention, and thus achieve the benefits disclosed herein, with the only stipulation being that inner sleeve 222 have an overall resulting thermal conductivity which is higher than that of outer sleeve 224.

Referring to Figure 17-19, in a further embodiment of the current invention, a film heater element is used to heat a manifold heater plate. Film heaters are known and have been used in many applications outside the injection molding process. Film heaters have been recently introduced in conjunction with hot runner injection nozzles and hot runner

15

20

25

30

manifolds. Reference is made in this regard to European Patent Application No. EP 0963829 to Husky Injection Molding Systems Ltd. and U.S. Patent No. 5,973,296 to Juliano et al., both incorporated herein by reference. Figure 17 shows a portion of a molding system M" having an infiltrated manifold 28" heated on one side by an element 36" and heated on the other side by an infiltrated manifold heater 50". A melt channel 12" though manifold 28" carries pressurized melt from the molding machine to an infiltrated nozzle 10". Referring to Figure 18, manifold heater 50" has a heater unit 300 attached thereto, the heater unit 300 comprising a film heater element 302 disposed between a dielectric layer 304 (which can also be a film layer) and an insulation layer 306. Referring to Figure 19, film heater element 302 is sheetlike having a heater element 308 and thermocouple element 310 therein. When activated, heater unit 300 provides heat to heater plate 50" which, in turn, heats manifold 28". The film heater shown in Fig. 18 and Fig. 19 can be manufactured using any known technology mentioned in EP 0963829 or U.S. Patent No. 5,973,296, and the references cited in both patents. It will be understood by one skilled in the art that heater 50" could equally be positioned between manifold 28" and nozzle 10", in a similar manner as shown in the embodiment of Figure 7, so as to perhaps remove the need for element 36"'.

Film heater technology can equally be used to provide an infiltrated band nozzle heater of the present invention (ie. of the type depicted in Figure 12). Referring to Figure 20, a film heater 320 is provided which comprises a film heater layer 322 between a dielectric layer 324 and an insulation layer 326, as described in U.S. Patent No. 5,973,296, and incorporated by reference. This heater provides heat to the infiltrated band heater 50"

Depending on a particular application, it may be desirable to employ a manifold, manifold heater plate and nozzle system in which some components are infiltrated and others are not. It is to be understood that the present invention includes all embodiments wherein at least one of said components is infiltrated.

15

20

25

30

In use, injection molding system M is assembled as shown in Figure 1. While only a single cavity 16 has been shown in Figure 1 for ease of illustration, it will be appreciated that melt distribution manifold 28, depending on the application, typically may have many melt passage branches extending to numerous cavities 16. Electrical power is applied to heating element 36 in manifold 28, and to heating elements 54 in the nozzles 10, to heat them to a predetermined operating temperature. Heating elements 36 in manifold 28 can be connected in series or in parallel. Alternatively, each heating element 36 or one or more groups of the heating elements 36 can be connected to a separately controlled power source (not shown) to individually adjust its temperature. In order to maintain the whole melt passage 12 at a uniform temperature it may be necessary to provide more heat to some manifolds 28 than to others. For instance, less heat is usually required for a manifold 28 in the centre of the mold 18 than for those around the periphery. Pressurized melt from a molding machine (not shown) is then injected into melt passage 12 through common inlet 40 according to a predetermined cycle in a conventional manner. pressurized melt flows through melt bore 42 of each nozzle 10, past torpedo 46 and through gate 14 to fill cavity 16. After cavities 16 are filled, injection pressure is held momentarily, to pack the part, and then released. After a predetermined cooling period, the mold is opened to eject the molded products. After ejection, the mold is closed and injection pressure is reapplied to refill cavities 16. This cycle is continuously repeated with a frequency dependent on the size and shape of cavities 16 and the type of material being molded.

As will be apparent to one skilled in the art, molding system M', as depicted in Figures 4 and 5, M", as depicted in Figure 12, and M" as depicted in Figure 17, operate substantially as just described, with the obvious exceptions. In the case of system M', heating elements 36', when activated, provide heat to heater plate 106 which, in turn heats manifold 28'. In the case of system M", heater 200 heats nozzle 10".

Due to the improved thermal conductivity characteristics of the

WO 01/54878 PCT/CA01/00092

- 15 -

infiltrated components according to the present invention, heat transferred from the heating element is more quickly and efficiently distributed through the infiltrated component by reason of the interconnected network of second phase metal 92 infiltrating the skeleton parent metal 90.

5

10

15

20

25

30

Thus, according to the present invention, by providing an injection molding component, such as manifold 28, heater plate 106, nozzle 10" or band heater 200, comprising a high-strength parent metal infiltrated by a second phase metal having high thermal conductivity, an injection molding component is achieved having high hardness, for withstanding high operation pressures and numerous operation cycles, and good thermal conductivity to effectively transfer heat throughout the structure. The result is improved temperature control of the pressurized melt within the manifold runner system, which can thereby beneficially affect cycle time, part quality and system efficiency.

According to the method of the present invention, manifold 28, front plate 114, rear plate 116, film heater plate 50", nozzle 10" and/or band heater 200 can be formed using metal infiltration techniques to yield a two phase metal part having high hardness and enhanced thermal properties. The following description relates to the practice of the method to form plates 114 and 116, but it will be understood that such description applies equally to the fabrication of manifold 28, heater 50", nozzle 10" and band heater 200, which contain modifications which will be evident to one skilled in the art.

A parent metal, typically a tool steel such as H13, is mixed in powder form with a plastic binder and prepared for metal injection molding into a preform having the near-net shape of a heater plate 114 or 116. It will be understood by one skilled in the art that the powder loading in the metal + binder admixture will be such that the green part will have shape retention when the part is debinderized. The admixture is then injection molded, using techniques well-known in the art, to yield a green part having a desired net or near-net shape.

The green part is next heated in a vacuum or inert gas environment to a temperature below the melting point of the parent metal

but above the melting point of the binder, to debinderize the preform and leave a green preform comprising a skeleton having interconnected open porosity. The porous preform is then partially sintered to decrease the porosity of the part, and create a sintered porous preform. As will be understood by the skilled artisan, an increase in sintering temperature correspondingly decrease the amount of porosity in the preform. Thus, as preservation of the interconnected porosity throughout the sintered preform is desired, the sintering temperature should not exceed the temperature at which pore closure is initiated. Preferably, the sintered preform will have a porosity of between 40% to 10% volume and, more preferably between 30% and 15%.

5

10

15

20

25

30

Referring to Figure 15, the porous preforms 114" and 116" of a front heater plate 114 and a rear heater plate 116, respectively, are then aligned and positioned with mating inner surfaces 114b and 116b adjacent one another, and with electrical heater element 36' positioned in channel 118 therebetween, to form a preform assembly 140. Terminals 36a of element 36 are left suitably exposed from preforms 114" and 116" for ultimate connection to a controlled power supply (not shown). The preform assembly 140 is then subjected to an infiltration of a second phase metal to substantially fill the porosity of the parent metal of heater plate preforms 114" and 116", as will now be described. A mass (not shown) of a thermally conductive metal, such as plate, sheet or ingot, is placed in contact with preforms 114" or 116", or both, of preform assembly 140 and then placed in a vacuum or inert gas furnace and heated to an infiltration temperature. The infiltrant mass need not contact both preforms 114" and 116", but need only contact one. In a particular application, however, a plurality on infiltrant masses may be desirable. The infiltration temperature of the furnace need only be slightly higher than the melting temperature of the metal infiltrant, and the infiltration temperature and time should generally be kept as low as possible to minimize any interaction or solubility between the parent metal and the At the infiltration temperature, the metal infiltrant melts infiltrant metal. over time and is absorbed by capillary action into the porous preform to fill

WO 01/54878 PCT/CA01/00092

the void spaces of the interconnected porosity therein. As will be apparent to one skilled in the art, sufficient infiltrant metal should be provided to substantially fill the interconnected porosity of the parent metal preform.

- 17 -

Advantageously, it has been found that as the second phase metal infiltrates into the interconnected porosity of the parent metal preform, the infiltrant also acts to braze faces 114b and 116b together. The infiltrant also simultaneously brazes electrical heating element 36' to channel 82. Thus, simultaneously with infiltration, an integral and metallurgically-bonded heater assembly 106 is achieved, thereby yielding good strength and thermal characteristics. Preferably, electrical heater element 36' is not infiltrated and the infiltration process does not otherwise affect the functionality of heater element 36.

10

15

20

30

Once infiltration is complete, the thermally conductive metal infiltrant fills the former interconnected porosity of the parent metal (see Figure 6). As a result, the manifold 28 and/or heater plate 106 has high hardness, for withstanding high operation pressures and numerous operation cycles, and good thermal conductivity to effectively transfer heat throughout the structure. The present invention also causes the thermally conductive metal infiltrant to set around electrical heating element 36', thereby integrating the element into heater plate 106 and thereby increasing the heat transfer efficiency of heater plate 106. The simultaneous nature of such brazing step beneficially reduces the number of steps required in tooling the molding system.

The present invention may be used advantageously with any parent metal having good strength characteristics, such as tool steels such as H13, M2, D2 or carbide steels. Regardless of parent metal chosen, the sintering conditions are used to control the amount of porosity in the green part, as one skilled in the art understands that overall porosity decreases with increased sintering temperature and/or time. Since the parent metal green preform must have connected open porosity, sintering must be carefully controlled to ensure that pore closure is avoided and the green part is permeable to the liquid metal infiltrant.

10

20

25

30

Any suitable metal infiltrant having high thermal conductivity may be successfully employed with the present invention. Copper and alloys of copper are most preferred, however.

It will be understood that binders suitable for use with the process of the present invention are those which melt or soften at low temperatures, such that the metal/binder admixture exhibits good flow properties during injection molding. However, the binder must also provide the green molded article with enough strength to prevent collapsing or deformation during handling. Preferably, the plastic binder chosen will degrade at a relatively low temperature to facilitate debinderization of the green part.

It will be apparent to one skilled in the art that the preform processing according to the present invention can be achieved through any powder processing method, and need not be limited to metal injection molding of the parent metal preform. For example, conventional powder pressing may be utilized, wherein the parent metal powder is first mixed with a lubricant, as is known in the art, and then pressed into the preform shape. The green preform is then delubed, and the porous preform is then sintered as described above. Alternatively, three-dimensional printing or other powder forming techniques as are known in the art may be employed. The present invention is not limited to a particular method of forming the parent metal preform and any method which yields a preform having interconnected open porosity may be employed.

The method of the present invention may be used to infiltrate and bond similar parent metals, for example such as in the joining of a heater plate 114 to a heater plate 116 as described above, or dissimilar metals, for example such as in the case of joining a heater element 36 to a heater plate 114 or 116, as described above, or both, as in the joining of heater plates 114 and 116 to heater element 36 as described above. The method may also be employed to create infiltrated injection nozzles, having integral heater elements simultaneously brazed therein during infiltration of the nozzle preform, as mentioned above. Similarly, other integrally heated components such as sprue bushings and the like may also be made according to the

WO 01/54878 PCT/CA01/00092

present method. Thus, the present invention may be employed with any number of porous preforms and any number of non-porous parts to be integrated therewith during infiltration.

- 19 -

Further, it will be understood by one skilled in that art that certain benefits may be achieved, depending upon the particular application, by using the teachings herein to fabricate a heater plate 106 according to the present invention in which only one of plates 114 and 116 is infiltrated according to the present invention and the other is uninfiltrated (see Figure 16, wherein plate 114 is uninfiltrated). Further, though advantageous, the simultaneous infiltration and brazing of plates 114 and 116 is not required to achieve benefit according to the present invention. It may also be desirable, in a particular application, to provide the Figure 7 embodiment with an infiltrated melt distribution manifold 100, in addition to or in place of, an infiltrated manifold heater. It will also be understood that it is not necessary that the infiltration within a particular part be uniformly distributed throughout the part, but rather may be localized in a region of the part. Likewise, it will be understood that plates 114 and 116 need not be composed of the same parent metals nor be infiltrated with the same second phase metals.

The following example is offered to aid understanding of the present invention and is not to be construed as limiting the scope of the invention as defined in the attached claims.

Example

5

10

15

20

25

A powder of H13 tool steel is mixed with a polymer binder. The admixture is then injection molded into a green part having the shape of front heater plate 114. The binder is thermally removed in a furnace, preferably at a temperature not exceeding 500°C, to yield a green preform having open and interconnected porosity. The green porous preform is then partially sintered in the range of 1150°C to 1260°C until a final porosity of the sintered part of between 40% to 10% by volume is achieved. Simultaneously or successively, an H13 porous preform for rear heater plate 116 is also created

15

using this described technique.

The front and rear heater preforms are fitted with a heater element 36' in recesses 114a and 116a and the preforms are then mated to yield a green heater assembly 140. The green assembly is then placed in a vacuum or inert gas furnace. A copper sheet is then placed on top of the green heater assembly, and the furnace is heated to 1120°C, slightly above the melting point of copper. The infiltrated and brazed integral part is then cooled and final machining, if any, is performed.

Thus it will be apparent to one skilled in the art the present invention provides an improved melt distribution manifold having improved strength and thermal characteristics over the prior art. Also, the method of the present invention provides simultaneous means of infiltrating and brazing a heated manifold assembly with heating element therein.

While the above description constitutes the preferred embodiments, it will be appreciated that the present invention is susceptible to modification and change without parting from the fair meaning of the proper scope of the accompanying claims.

WO 01/54878 PCT/CA01/00092

CLAIMS:

1. An assembly for heating an injection molding component, the assembly comprising:

- 21 -

- (a) a body; and
- 5 (b) a heating element attached to said body for controllably heating said body,

wherein said body is made of a parent metal, said parent metal being at least partially infiltrated with a second metal, said second metal having a higher thermal conductivity than said parent metal.

- 10 2. An assembly according to claim 1 said body further comprising a groove, and wherein said heating element is disposed in said groove.
 - 3. An assembly according to claim 1 wherein said body is a melt distribution manifold for transferring molten resin from an injection molding machine to at least one injection nozzle.
- 4. An assembly according to claim 1 wherein said body is a heater for heating a melt distribution manifold.
 - 5. An assembly according to claim 1 wherein said body is an injection molding nozzle.
- 6. An assembly according to claim 1 wherein said body is a heater for20 heating an injection molding nozzle.
 - 7. An assembly according to claim 4 wherein said body is planar.
 - 8. An assembly according to claim 6 wherein said body is annular.
 - 9. An assembly according to claim 1 wherein said body comprises a first

PCT/CA01/00092 WO 01/54878

member and a second member and wherein said heating element is disposed substantially between said first and second members.

- 22 -

- 10. An assembly according to claim 1 further comprising a second body attached to said body.
- 5 An assembly according to claim 10 wherein said second body is made 11. of an uninfiltrated metal.
 - 12. An assembly according to claim 1 wherein said heating element is joined to said body by brazing.
- An assembly according to claim 12 wherein said element is brazed 13. 10 using said second metal.
 - An assembly according to claim 1 wherein said heating element is an 14. electrical resistance type heater.
 - 15. An assembly according to claim 1 wherein said heating element is a film heater.
- 15 16. An assembly according to claim 1 wherein said heating element is a passage through which a heated fluid is circulated.
 - An assembly according to claim 1 wherein said heating element is 17. attached to said body by a friction fit.
- An assembly according to claim 1 wherein said heating element is 18. 20 attached to said body by thermal spraying.
 - 19. An assembly according to claim 1 wherein said parent metal is a tool steel.

15

- 20. An assembly according to claim 1 wherein said second metal is chosen from the group of copper, copper alloys, silver and silver alloys.
- 21. An assembly according to claim 1 wherein said second metal comprises between 40%-volume and 10%-volume of said body.
- 5 22. A hot runner injection molding apparatus comprising:
 - (a) a melt conveying system, said system having
 - a melt distribution manifold having at least one melt passage for transferring melt from a source of pressurized melt, and
 - (ii) at least one injection nozzle having a melt bore therethrough, said melt bore in fluid communication with said at least one manifold melt passage
 - (b) at least one mold cavity adjacent said at least one nozzle, said mold cavity in fluid communication with said melt bore of said at least one nozzle.
 - (c) a body for heating at least a portion of said melt conveying system, said body having a heating element attached thereto, said heating element capable of heating at least a portion of said body;

wherein at least a portion of said body is made of a parent metal, said
20 parent metal being at least partially infiltrated with a second metal having a
higher thermal conductivity than said parent metal.

- 23. An apparatus according to claim 22 wherein said body is a heater for heating said melt distribution manifold.
- 24. An apparatus according to claim 23 wherein said body is planar.
- 25 25. An apparatus according to claim 22 wherein said body is a heater for heating said at least one nozzle.

15

20

- 26. An apparatus according to claim 25 wherein said body is annular.
- 27. An assembly according to claim 22 wherein said heating element is disposed interior of said body.
- 28. A process for fabricating an injection molding component having an electrical heating element attached thereto, the process comprising the steps of:
 - (a) contacting said electrical heating element with a powdered metal preform having at least partial open porosity, said powdered metal preform being composed of a first metal;
 - (b) contacting said preform adjacent a region of said open porosity with a mass of a second metal, said second metal having higher thermal conductivity than said first metal;
 - (c) heating said preform, said heating element and said mass so as to cause said second metal to at least partially infiltrate said open porosity of said preform and at least partially join said heating element to said preform when cooled.
 - 29. A process for fabricating a metal part having at least two components, the process comprising the steps of:
 - (a) making a powdered preform of a first component, said preform having at least partial open porosity;
 - (b) contacting a second component with said preform of said first component; and
- (c) infiltrating said open porosity of preform with a second metal wherein said second component is brazed to said first component by
 said second metal substantially contemporaneously with said infiltration step.
 - 30. A process for fabricating a metal part having at least two components, the process comprising the steps of:

PCT/CA01/00092 WO 01/54878

(a) making a powdered preform of a first component, said preform having at least partial open porosity;

- 25 -

- (b) contacting a second component with said preform of said first component to form an assembly thereof;
- 5 (c) contacting said preform first component with a mass of a metal infiltrant;
 - (d) controllably heating said assembly and said metal infiltrant to melt said metal infiltrant;
- (e) holding said assembly and said metal infiltrant at temperature until 10 said open porosity of said preform of said first component is at least partially infiltrated by said metal infiltrant and said second component is at least partially brazed to said first component by said metal infiltrant; and
 - (f) controllably cooling said assembly to solidify the metal infiltrant.
 - The process of claim 30 further comprising the steps of: 31.
 - (a) providing said first component by:

15

20

- (i) mixing a metal powder with a binder to form an admixture;
- (ii) injection molding said admixture into a preform;
- (iii) heating said preform to extract said binder from said binder, thereby leaving said preform with open porosity; and
- partially sintering said preform to partially reduce said (iv) open porosity.
- The process of claim 30 wherein said second component is substantially 32. 25 impermeable to said metal infiltrant.
 - The process of claim 32 wherein said second component is a resistance 33. heater element.
 - The process of claim 30 wherein said second component is a green 34.

powder preform having at least partial open porosity, such that said second component is capable of being infiltrated by said metal infiltrant.

- 35. The process of claim 34 wherein said first and second components are matable heater plates for a manifold heater.
- 5 36. The process of claim 30 wherein said metal infiltrant is a material having high thermal conductivity.
 - 37. The process of claim 30 wherein said metal infiltrant is substantially copper.
- 38. The process of claim 30 wherein said first component is made of a high strength metal alloy.
 - 39. The process of claim 38 wherein said first component is made of a tool steel.
 - 40. The process of claim 31 wherein said first component is made of a tool steel.
- 15 41. The process of claim 40 wherein the binder is extracted at a temperature not exceeding 500°C
 - 42. The process of claim 40, wherein the preform is partially sintered at a temperature between 1150°C and 1260°C
- 43. The process of claim 40, wherein said first component porosity20 comprises between 40 to 10% volume of said first component prior to infiltration.
 - 44. The process of claim 30 wherein said infiltration is localized over a

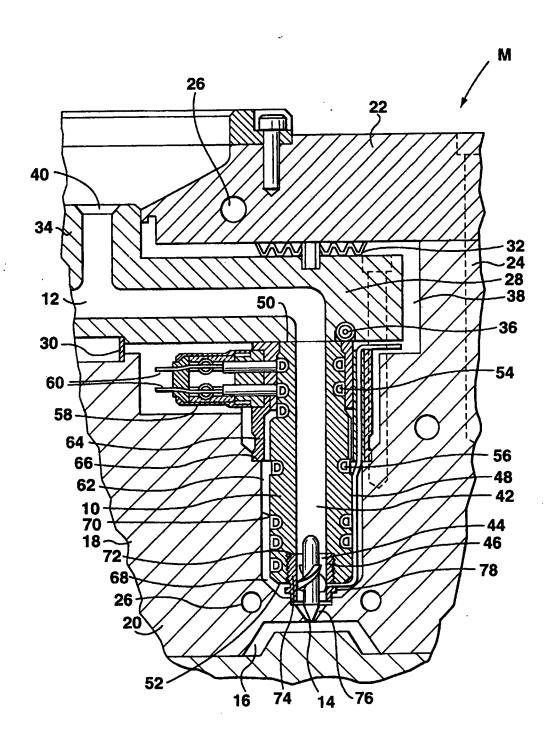
15

region of said first component.

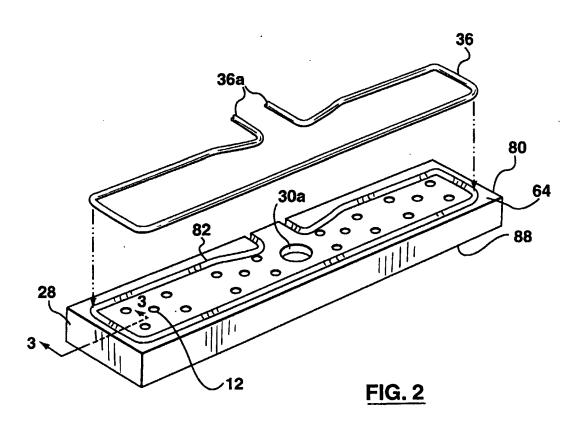
- 45. A process for fabricating an injection molding component, the process comprising the steps of:
 - (a) mixing a powdered tool steel with a binder to form an admixture;
 - (b) injecting said admixture into a preform;
 - (c) debinderizing said preform;
 - (d) partially sintering said preform to achieve 40% to 10% volume open porosity therein;
- 10 (e) contacting said preform with a metal infiltrant, said metal infiltrant having high thermal conductivity;
 - (f) controllably heating said preform and said metal infiltrant to at least the melting temperature of said metal infiltrant;
 - (g) holding said preform and said metal infiltrant at temperature until said porosity of said first component is at least partially infiltrated by said metal infiltrant; and
 - (h) cooling said preform to solidify the metal infiltrant and yield said injection molding component.
- 20 46. The process of claim 45 wherein steps (a)-(d) are repeated prior to step (e) to form a second preform and wherein said second preform is contacted with the first preform in step (e) such that said second preform is at least partially infiltrated by said metal infiltrant in steps (f)-(h) to yield a second manifold heater plate.
- 25 47. The process of claim 46 wherein said manifold heater plate and said second manifold heater plate are also brazed together by the performance of steps (e) (h).
 - 48. The process of claim 47 wherein step (e) further comprises providing a heater element and contacting said heater element to said preform and said

second preform.

49. The process of claim 48 wherein said heater element is brazed to at least said manifold heater plate by the performance of steps (e) - (h).



2/13



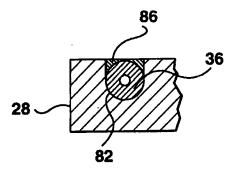
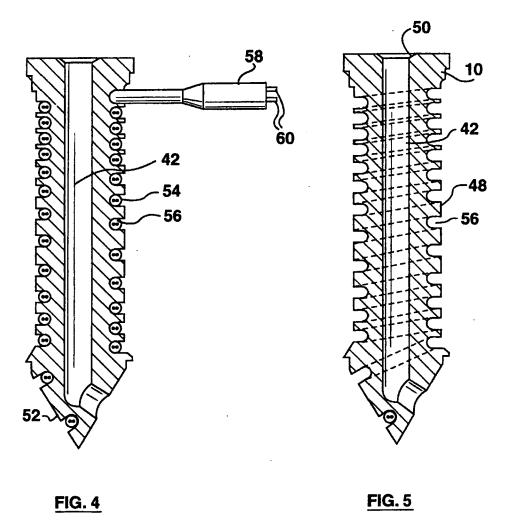


FIG. 3



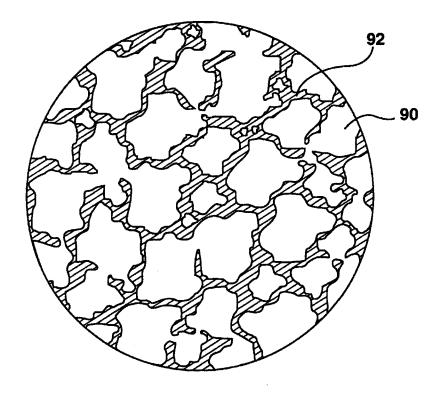
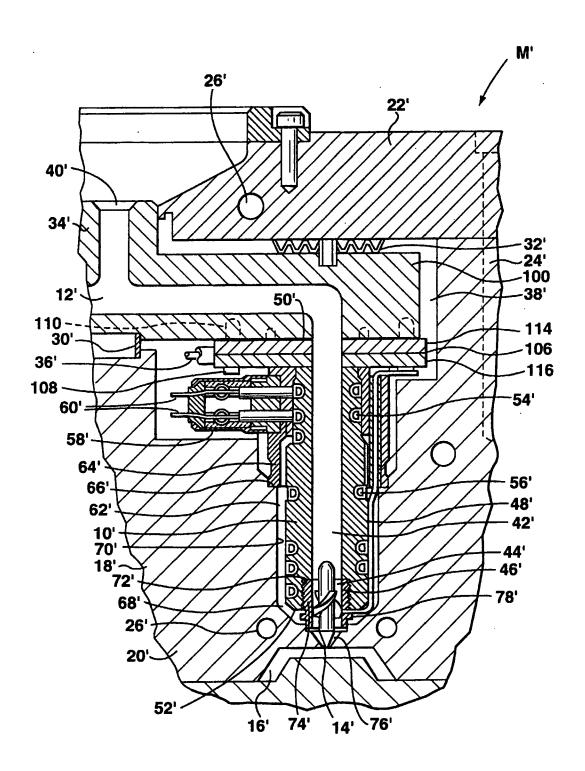
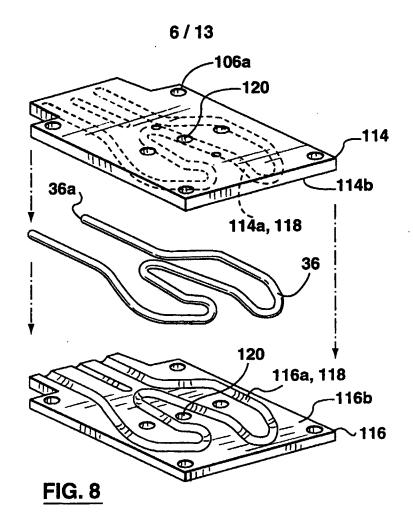


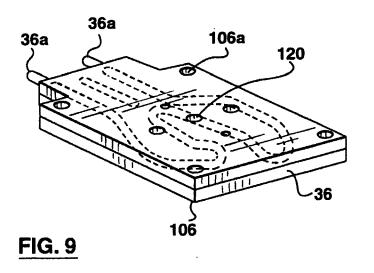
FIG. 6



SUBSTITUTE SHEET (RULE 26)

PCT/CA01/00092





SUBSTITUTE SHEET (RULE 26)

7/13

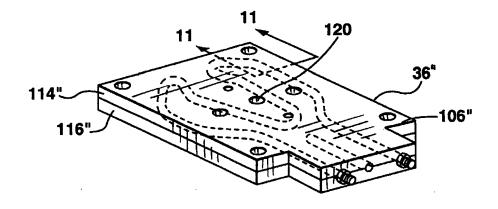


FIG. 10

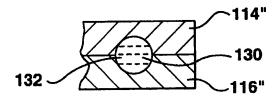


FIG. 11

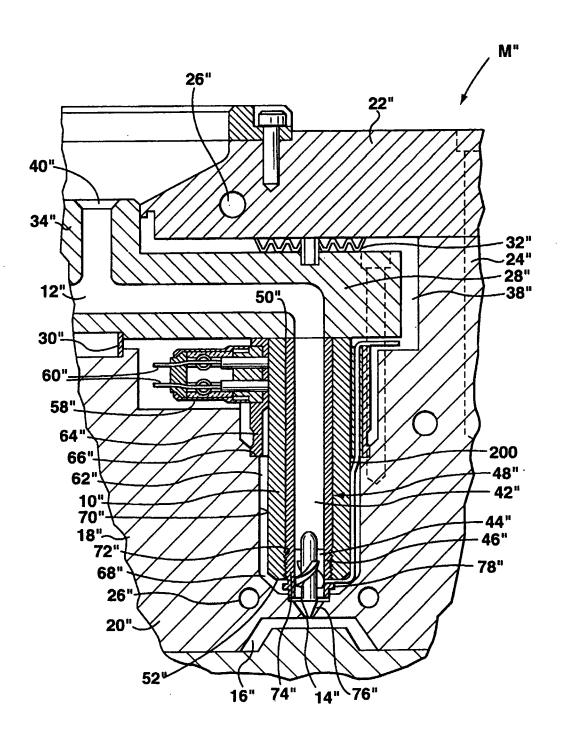
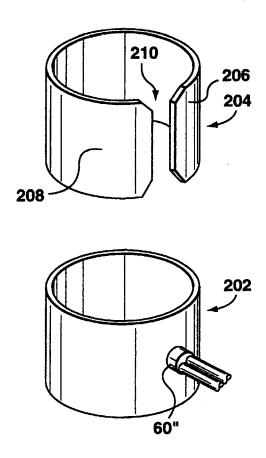


FIG. 12

9/13



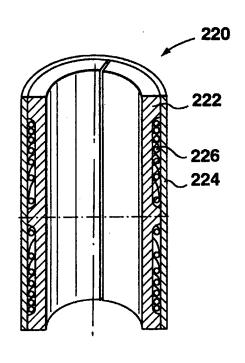


FIG. 13

FIG. 14

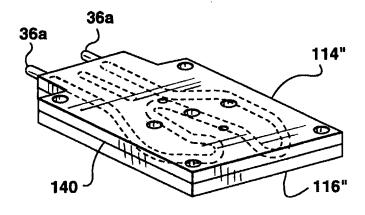


FIG. 15

11/13

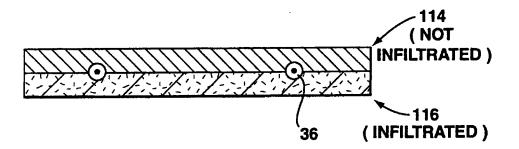


FIG. 16

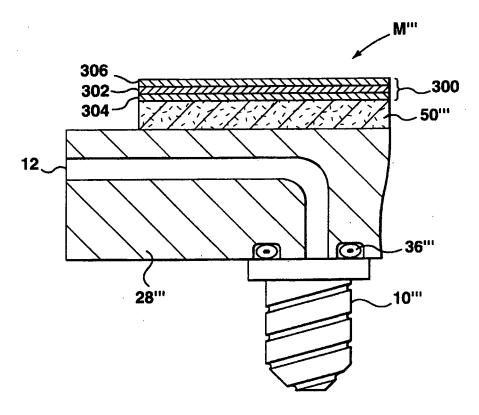


FIG. 17

12/13

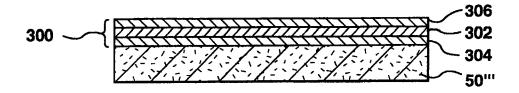


FIG. 18

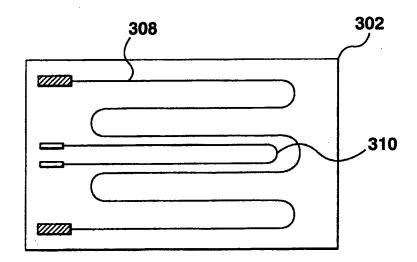


FIG. 19

13/13

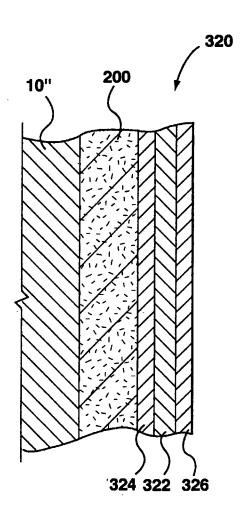


FIG. 20

INTERNATIONAL SEARCH REPORT

In al Application No PCT/CA 01/00092

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B29C33/38 B29C45/27
B29C45/73, B22F3/26

B22F5/00

//B29C33/02,B29C45/26,

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

 $\begin{tabular}{ll} Minimum documentation searched (classification system followed by classification symbols) \\ IPC 7 B29C B23P B22F C23C \\ \end{tabular}$

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
х	US 4 455 353 A (BRUCE LARS M) 19 June 1984 (1984-06-19)	1-21, 28-49
Y	column 5, line 9 -column 6, line 54; figures 1,2	22-27
X	US 5 507 336 A (TOBIN JAMES R) 16 April 1996 (1996-04-16)	1-21, 28-49
'	column 5, line 6 - line 30; figure 8 column 6, line 37 - line 40; figures 14,15	22-27
'	EP 0 681 899 A (MOLD MASTERS LTD) 15 November 1995 (1995-11-15) column 7, line 13 -column 8, line 31; figures	22–27
	-/	

Further documents are listed in the continuation of box C.	γ Patent family members are listed in annex.
*Special categories of cited documents: *A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority clalm(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed	 "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family
Date of the actual completion of the international search	Date of mailing of the international search report
31 May 2001	22/06/2001
Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Topalidis, A

INTERNATIONAL SEARCH REPORT

In onal Application No
PCT/CA 01/00092

		PC1/CA 01/00092						
C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT								
Category °	Citation of document, with indication, where appropriate, of the relevant passages		Relevant to claim No.					
Y	US 5 437 093 A (GELLERT JOBST U) 1 August 1995 (1995-08-01) column 4, line 23 -column 5, line 26; figures		22-27					
A	US 4 203 197 A (CRANDELL WALTER R) 20 May 1980 (1980-05-20) column 3, line 25 -column 4, line 11; claim 1; figures		1-21, 28-49					
A	US 4 314 399 A (SEVERINSSON LARS M) 9 February 1982 (1982-02-09) column 3, line 7 -column 4, line 34; figures column 6, line 8		1-21, 28-49					
1.								
	•							
	. •							
*	;							
, 4								
•								
:								

INTERNATIONAL SEARCH REPORT

information on patent family members

pcT/CA 01/00092

Patent document cited in search report	t	Publication date		ratent family member(s)	Publication date
US 4455353	Α	19-06-1984	SE	426662 B	07-02-1983
03 4433333	^	15 00 150 .	ĀŤ	376920 B	25-01-1985
			ΑŤ	913680 A	15-06-1984
			ΑÚ	6709481 A	17-08-1981
			CH	657793 A	30-09-1986
					25-03-1982
			DE	3050243 T	03-02-1982
			EP	0044841 A	
			PT	72399 A,B	01-02-1981
			WO	8102126 A	06-08-1981
		_	SE	8000799 A	02-08-1981
US 5507336	 А	16-04-1996	AT	195681 T	15-09-2000
00 000,000	• •		AU	709888 B	09-09-1999
			AU	4750896 A	07-08-1996
			BR	9606764 A	06-01-1998
			CA	2210537 A	25-07-1996
			CN	1168115 A	17-12-1997
			DE	69609945 D	28-09-2000
				69609945 T	08-02-2001
			DE		12-11-1997
			EP	0805729 A	16-02-2001
			ES	2153092 T	
			JP	10512328 T	24-11-1998
			KR	253972 B	15-04-2000
		·	WO	9622170 A	25-07-1996
EP 0681899	Α	15-11-1995	CA	2123472 A	13-11-1995
2. 00			US	5496168 A	05-03-1996
			DE	19516792 A	16-11-1995
			JP	8039640 A	13-02-1996
US 5437093	Α	01-08-1995	NONI		
US 4203197	Α	20-05-1980	CA	1100560 A	05-05-1981
00 4500131	• •		GB	1583771 A	04-02-198
		•	GB	1583772 A	04-02-1983
			GB	1583773 A	04-02-198
US 4314399	Α	09-02-1982	SE	411306 B	17-12-1979
03 4314323	М	09 02 1902	AU	2176877 A	03-08-1978
			CA	1128274 A	27-07-1982
			DE	2702602 A	04-08-197
			DK	35777 A	29-07-197
				2339465 A	26-08-197
			FR		01-10-198
			GB	1576222 A	
			IT	1076343 B	27-04-198
			JP	52115860 A	28-09-197
			NL	7700925 A	01-08-197
			PT	66114 A,B	01-02-197
			SE	7600895 A	29-07-197 27-07-198
				63483 G	